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Synthesis of a Polymer Surface Containing Covalently Attached Triethoxysilane Functionality: Adhesion to Glass

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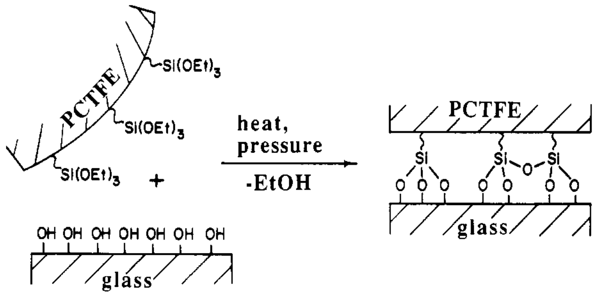
ABSTRACT: The reaction of poly(chlorotrifluoroethylene) film containing surface hydroxyl groups (PCTFE–OH) with (3-isocyanatopropyl)triethoxysilane in the presence of dibutyltin dilaurate produces a polymer surface containing alkyltriethoxysilane functionality (PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$). ATR IR and XPS results indicate that the reaction proceeds in essentially quantitative yield and that the triethoxysilane moiety is intact and covalently attached to the polymer film surface via a urethane linkage. Acid-catalyzed hydrolysis of PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$ yields a surface containing both siloxane and silanol functionality: PCTFE–OC(O)NH$(CH_2)_3$Si(O)OH. PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$ adheres tenaciously to glass slides; when placed in contact with glass under mild heat (80 °C) and pressure, the polymer film (5 mil) cannot be removed from the glass without tearing the film. SEM and XPS analyses of the glass surface indicate that cohesive failure in PCTFE occurs on delamination. PCTFE, PCTFE–OH, and PCTFE–OC(O)NH$(CH_2)_3$Si(O)OH films do not adhere to glass under the same conditions. PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$ and PCTFE–OC(O)NH$(CH_2)_3$SiO(O)OH films adhere to themselves, each other, and PCTFE–OH. The adhesive bonds are relatively weak, and apparent adhesive failure occurs on separation. PCTFE–OH film does not autoadhere.

Introduction

The preparation of polymer surfaces containing well-defined chemical compositions with specific functional groups in specific locations and densities is an objective we began[2-7] with the hope of preparing substrates suitable as models for drawing surface structure–property and –reactivity correlations. We chose to study chemically resistant (unreactive) polymers with versatilely reactive organic functional groups at their surfaces for reasons already described.[5] Challenging questions in this research are the following: Can we predict properties knowing the surface–chemical structure? Can we design and prepare surfaces with desired properties? We have reported water contact angle data for over 30 surfaces,[2-7] and with regard to one property, wettability, the answer to these questions is yes, reasonably well.

This paper reports work that had as an objective the design and synthesis of a polymer film surface which would form a strong adhesive bond to glass. The strategy we used involves silane coupling agent chemistry[8,9] applied so as to be suitable for solid–solid interface synthesis (eq 1).



(1)

Experimental Section

Materials. PCTFE was obtained from Allied as 5-mil film (Aclar 33C), extracted with refluxing dichloromethane for 15 min, and dried (0.02 mm, 70 °C) for at least 24 h. This procedure gives samples consistently free of detectable contaminants. Glass microscope slides (Fisher) were stored in KOH/2-isopropanol solution for 24 h and then washed with water, methanol, and dichloromethane, in this order, and dried at reduced pressure (0.02 mm). Tetrahydrofuran was distilled from sodium benzophenone dianion; dichloromethane was distilled from calcium hydride. House distilled water was redistilled by using a Gilmont still. All solvents were stored under nitrogen. Dibutyltin dilaurate (Aldrich) and (3-isocyanatopropyl)triethoxysilane (Petrarch) were used as received.

Methods. Air-sensitive reactions were carried out under dry nitrogen. Reactions with films were not stirred. Contact angle measurements were obtained with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24 gauge flat-tipped needle. Water purified as described above was used as the probe fluid. Dynamic advancing and receding angles were determined by measuring the tangent of the drop at the intersection of the air/drop/surface while adding (advancing) and withdrawing (receding) water to and from the drop. The values reported are averages of five measurements made on different areas of the film sample surface. Attenuated total reflectance infrared (ATR IR) spectra were obtained under nitrogen by using an IBM 38 FTIR spectrometer and a germanium (45°) internal reflection element. The absorbances listed in the Experimental Section do not include bands due to PCTFE and PCTFE–OH and include bands between 4000 and 700 cm^{-1}. X-ray photoelectron spectra (XPS) were recorded by using a Perkin Elmer–Physical Electronics 5100 spectrometer with Mg Kα excitation (300 W). The samples charged variably during analysis, and the reported binding energies are not corrected for charging. Spectra were recorded with the analyzer positioned 75° from the film surface. Atomic composition data were determined by using the instrument's computer and programmed sensitivity factors: F_{1s}, 1.00; O_{1s}, 0.66; N_{1s}, 0.42; C_{1s}, 0.25; Cl_{2p}, 0.73; Si_{2p}, 0.27. Scanning electron microscopy (SEM) (secondary electron images) was performed on JEOL 60 SEM and JEOL 100 STEM instruments. Adhesive joint formation experiments were carried out in air with a Carver Laboratory Press.

Hydroxylated Poly(chlorotrifluoroethylene) (PCTFE–OH). PCTFE–OH film samples were prepared as previously reported.[7] Conditions to prepare 50- and 1500-Å-thick modified surfaces were reproduced.

Preparation of PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$. PCTFE–OH film samples were placed in a Schlenk tube which was then purged with nitrogen for 20 min. THF (20 mL) was added via cannula, and then dibutyltin dilaurate (0.032 mg, 0.05 mmol) and (3-isocyanatopropyl)triethoxysilane (0.50 g, 2.02 mmol) were added via syringe. The reaction was allowed to proceed for 24 h, after which time the reaction solution was removed via cannula. The film samples were washed under nitrogen with THF (3 × 20 mL) and then dichloromethane (3 × 20 mL) and dried at reduced pressure (0.02 mm, 24 h). ATR IR 3450 (w, sh), 3341 (m), 2975 (s), 2923 (s), 2888 (s), 1723 (s, sh), 1703 (s), 1534 (s), 1478 (w), 1445 (m), 1412 (w), 1391 (m), 1366 (w), 1246 (s), 1167 (s), 1105 (s, sh), 1078 (s), 793 (m, sh), 777 (s), 741 (s), 704 (w) cm^{-1}. XPS atomic ratios calcd for $C_{62}F_6O_{20}N_4Si_4$: C, 65; F, 6; O, 21; N, 4; Si, 4. Obsd: C, 64; F, 7; O, 22; N, 4; Si, 4.

Hydrolysis of PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$. PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$ film samples were stored in 0.05 M HCl (water/methanol 1:1) at room temperature for 24 h. The acid solution was removed, and the film samples were washed

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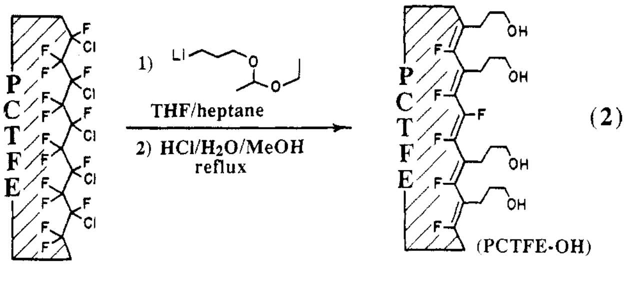
with water (3 × 20 mL), methanol (3 × 20 mL), and dichloromethane (3 × 20 mL), in this order, and dried at reduced pressure. Contact angles θ_A/θ_R = 51°/22°. ATR IR 3337 (s, br), 2940 (m), 2888 (w), 1698 (s), 1532 (s), 1449 (w), 1250 (s), 1055 (s), 777 (w) cm^{-1}. XPS atomic ratios calcd for $C_{38}F_6O_{16}N_4Si_4$ (PCTFE-OC(O)NH$(CH_2)_3$Si(O)OH): C, 56; F, 9; O, 24; N, 6; Si, 6. Obsd: C, 58; F, 6; O, 22; N, 6; Si, 8.

Adhesive Joint Formation Experiments. A film sample was placed on a microscope slide, and 10-mil Mylar films were placed over the film and under the glass (this prevented the glass from breaking). The sandwich was placed in a hydraulic press at 80 °C, and 500 psi was applied. The pressure was maintained for 3–5 h, and then it was allowed to decrease (to <100 PSI) for the next 7–9 h. The sample was taken out of the press and allowed to cool to room temperature. Polymer–polymer adhesive joint experiments were performed identically.

Results and Discussion

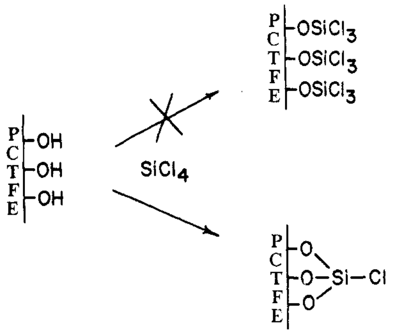
Hydroxylated poly(chlorotrifluoroethylene) (PCTFE–OH) was prepared by using 5-mil PCTFE film and conditions which render modified film thicknesses of ~50 and ~1500 Å.[5,7] This chemistry and the structure of the modified surface are summarized in eq 2.



(2)

Quantitative XPS analyses of PCTFE–OH, its precursor (the ethyl vinyl ether protected alcohol), and a range of derivatives indicate that PCTFE–OH contains four hydroxyl groups per five repeat units of modified PCTFE.[7] The fifth repeat unit is a difluoroolefin. The 50- and 1500-Å-thick modified surfaces are identical by XPS, which analyzes the outer ~40 Å of the film sample. All of the data reported here are for 1500-Å-thick modified film samples; these samples allow ATR IR analysis of reactions. Each of the reactions and adhesion experiments reported were also carried out on 50-Å-thick modified surfaces: identical XPS, contact angle, and adhesion behavior were observed, but infrared spectra were not useful.

PCTFE–OH was chosen as a starting material because its chemistry is most developed among surface substrates. A complexity of its chemistry that had to be overcome to prepare a surface containing silane coupling agents is its tendency to react multiply with multifunctional reagents. Adipoyl chloride and 1,6-hexanediisocyanate react to form predominantely the diester and diurethane, respectively, even when present in large excess.[7] The alkoxytrichlorosilane surface cannot be prepared (eq 3) by reaction with tetrachlorosilane; instead, the trialkoxychlorosilane is the predominant product.[7]



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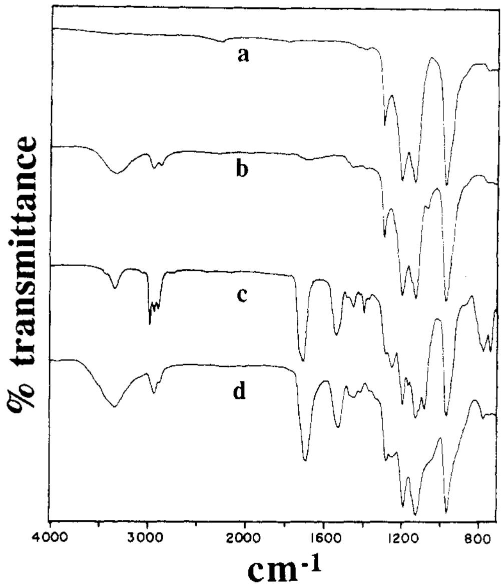
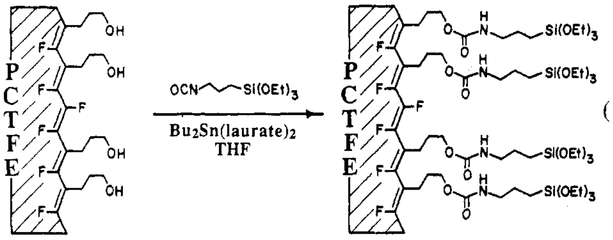


Figure 1. ATR IR spectra of PCTFE (a), PCTFE–OH (b), PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$, (c) and PCTFE–OC(O)NH$(CH_2)_3$Si(O)OH (d).

A difunctional reagent containing both a silane coupling agent (or precursor) that does not react with PCTFE–OH and a functional group that does react with PCTFE–OH was needed.

Preparation of PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$. The reaction of PCTFE–OH with (3-isocyanatopropyl)triethoxysilane in the presence of dibutyltin dilaurate (a urethanation catalyst) in THF at room temperature for 24 h yields PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$ (eq 4).



(4)

The urethane is the sole product of this reaction; the triethoxysilane moiety does not condense with surface hydroxyl groups under these conditions.[10] The ATR IR spectrum (Figure 1c) indicates reaction of the hydroxyl groups in PCTFE–OH (loss of broad O–H band at 3335 cm^{-1}, Figure 1b) and the presence of two N–H stretching modes (3450 cm^{-1} (free N–H) and 3341 cm^{-1} (hydrogen-bonded N–H)), three C–H stretching bands (2975, 2923, and 2888 cm^{-1}), two carbonyl bands (1723 cm^{-1} (free) and 1703 cm^{-1} (hydrogen-bonded)), a coupled N–H/C–N deformation (1534 cm^{-1}), various C–H bending modes (1478, 1445, 1412, 1391, and 1366 cm^{-1}), a $SiCH_2$ deformation (1246 cm^{-1}), and Si–O–C stretching bands (1167, 1105, and 1078 cm^{-1}). The XPS spectrum (Figure 2c) displays the expected photoelectron lines corresponding to F_{1s} (692 eV), O_{1s} (537 eV), N_{1s} (404 eV), C_{1s} (290 eV), and Si_{2p} (107 eV). The observed atomic ratios match well with those calculated for the proposed structure (Table I). Figure 3 displays the high-resolution C_{1s} spectrum of PCTFE-OC(O)NH$(CH_2)_3$Si$(OEt)_3$ curve-fitted with three peaks. We assign the high binding energy peak to the carbonyl carbons (indicated by ▲ in the figure), the middle binding energy peak to the carbons bound to N, O, or F(■), and the low binding energy peak to the remaining carbons (●). This rather crude curve fitting agrees fairly well with the structure: the observed area percentages of the ▲, ■, and

Table I
XPS Atomic Composition Data

		calculated, %						observed, %					
sample	empirical formula	C	F	O	N	Cl	Si	C	F	O	N	Cl	Si
PCTFE	C_2F_3Cl	33	50	0	0	17	0	34	51	<1	0	15	0
PCTFE–OH	$C_{22}F_6O_4$	69	19	13	0	0	0	69	16	15	0	0	0
PCTFE–OC(O)NH(CH_2)$_3$Si(OEt)$_3$	$C_{62}F_6O_{20}N_4Si_4$	65	6	21	4	0	4	64	7	22	4	0	4
PCTFE–OC(O)NH(CH_2)$_3$Si(O)OH[a]	$C_{38}F_6O_{16}N_4Si_4$[a]	56	9	24	6	0	6	58	6	22	6	0	8
PCTFE–OC(O)NH(CH_2)$_3$Si(OH)$_3$[b]	$C_{38}F_6O_{20}N_4Si_4$[b]	53	8	28	6	0	6						
PCTFE–OC(O)NH(CH_2)$_3$Si(O)$_{1.5}$[c]	$C_{38}F_6O_{14}N_4Si_4$[c]	58	9	21	6	0	6						

[a] Assuming two-thirds of hydroxyl groups have condensed to siloxanes. [b] Assuming all hydroxyl groups are intact. [c] Assuming all hydroxyl groups have condensed to siloxanes.

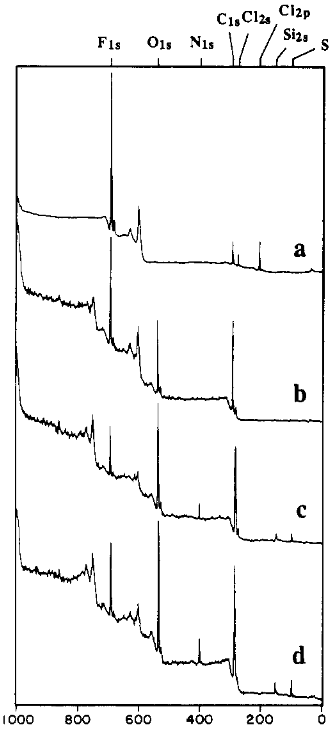


Figure 2. XPS survey spectra of PCTFE (a), PCTFE–OH (b), PCTFE–OC(O)NH(CH_2)$_3$Si(OEt)$_3$ (c), and PCTFE–OC(O)NH(CH_2)$_3$Si(O)OH (d).

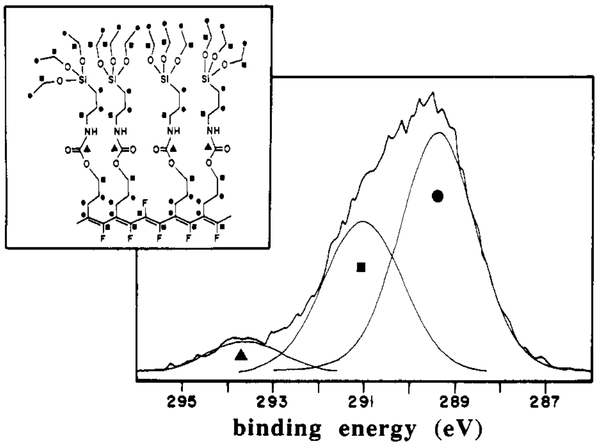


Figure 3. C_{1s} region of XPS spectrum of PCTFE–OC(O)NH(CH_2)$_3$Si(OEt)$_3$.

● peaks are 7%, 36%, and 57%, respectively; the values calculated on the basis of the structure are ▲, 6%; ■, 42%; and ●, 52%. PCTFE–OC(O)NH(CH_2)$_3$Si(OEt)$_3$ film samples were to hygroscopic; meaningful contact angle data could not be obtained.

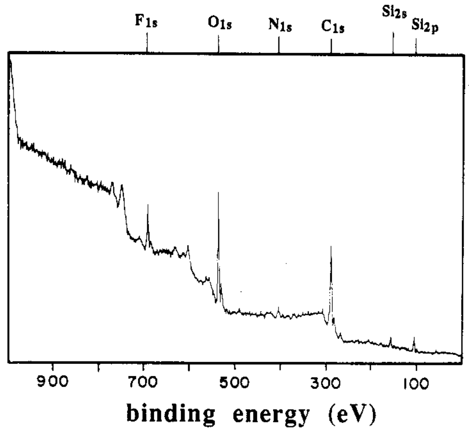
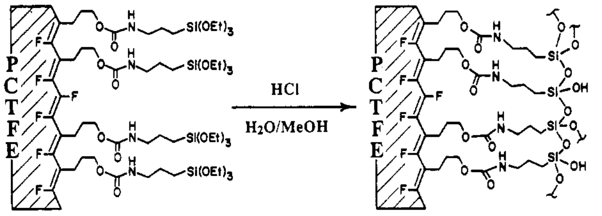


Figure 4. XPS survey spectrum of the glass slide after PCTFE–OC(O)NH(CH_2)$_3$Si(OEt)$_3$ has been peeled off.

Hydrolysis of PCTFE–OC(O)NH(CH_2)$_3$Si(OEt)$_3$. Treatment of PCTFE–OC(O)NH(CH_2)$_3$Si(OEt)$_3$ with 0.05 M HCl in methanol/water (1:1) at room temperature for 24 h produces changes in the film surface consistent with hydrolysis and formation of a cross-linked siloxane surface containing silanol functionality (eq 5).



(5)

The presence of the cross-linked siloxane structure as the major feature (and not a preponderance of PCTFE–OC(O)NH(CH_2)$_3$Si(OH)$_3$) is indicated by XPS data (Figure 2d, Table I). The calculated oxygen concentration for PCTFE–OC(O)NH(CH_2)$_3$Si(OH)$_3$ is 28%, for PCTFE–OC(O)NH(CH_2)$_3$SiO(OH) (two-thirds dehydrated) is 24%, and for PCTFE–OC(O)NH(CH_2)$_3$–SiO$_{1.5}$ (completely dehydrated) is 21%. The observed oxygen concentration is 22%, suggesting a highly cross-linked siloxane surface. The ATR IR spectrum of PCTFE-OC(O)NH(CH_2)$_3$Si(O)OH (Figure 1d) displays a broad O–H stretching band (3337 cm^{-1}) that obscures the N–H bands, two methylene bands (2940 and 2888 cm^{-1}), a carbonyl stretching band (1698 cm^{-1}), a N–H/C–N coupled deformation (1532 cm^{-1}), and a Si–CH_2 deformation band (1250 cm^{-1}). The intense O–H stretching band suggests that silanol functionality is an important structural feature (more important than the XPS data suggest), but this may be due, in part, to water adsorbed on the surface. The contact angles are low, θ_A/θ_R = 51°/22°, indicating a very hydrophilic surface. We use the abbreviation PCTFE–OC(O)NH(CH_2)$_3$SiO(OH) to indicate the hydrolysis product and that both siloxane and silanol functionality are present; this may not accurately

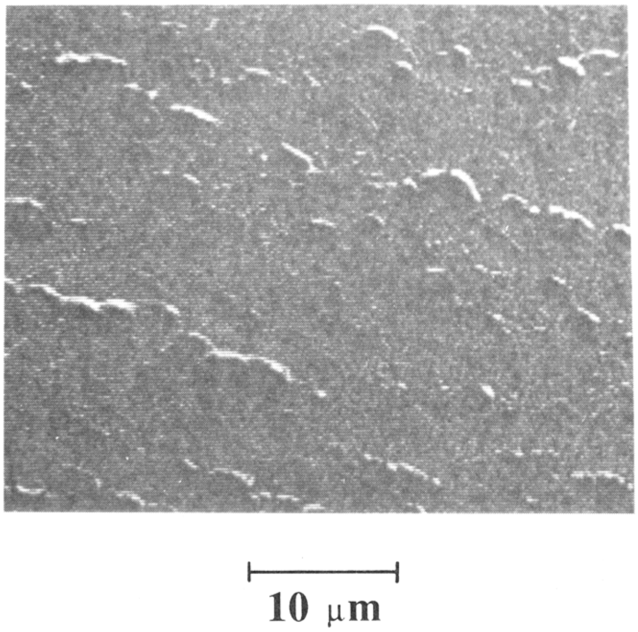


Figure 5. SEM of the glass slide after PCTFE–OC(O)NH-$(CH_2)_3Si(OEt)_3$ has been peeled off.

indicate the compositional structure.

PCTFE–OC(O)NH$(CH_2)_3$Si(OEt)$_3$—Glass Adhesion. Attempts to form adhesive joints between polymer films and glass were carried out between Mylar film in a laboratory hydraulic press with applied heat and pressure. PCTFE, PCTFE–OH, and PCTFE–OC(O)NH$(CH_2)_3$Si(O)OH show no tendency to adhere to glass under various experimental conditions varying from 80 to 120 °C for up to 24 h. Polymer films fell when the glass slide was inverted. PCTFE–OC(O)NH$(CH_2)_3$Si(OEt)$_3$ samples, on the other hand, adhere tenaciously to glass when bonding was carried out at 80 °C for 12 h. The film could not be peeled from the glass without tearing it, indicating cohesive failure in the polymer film. XPS and SEM of glass surfaces after the films were peeled also indicate cohesive failure in the polymer (Figures 4 and 5).

We ascribe the adhesive bond strength between the polymer film sample and glass to covalent bonds. The evidence that covalent bonding exists between the polymer film and the coupling agent through a urethane linkage is strong, indicated by spectroscopic characterization of PCTFE–OC(O)NH$(CH_2)_3$Si(OEt)$_3$. We have no direct evidence confirming that condensation between polymer surface Si(OEt)$_3$ groups and glass Si–OH groups occurs (eq 1). The control experiments with PCTFE–OH and PCTFE–OC(O)NH(CH_2)3Si(O)OH (which have no surface Si(OEt)$_3$ groups), however, indicate that this condensation is the likely source of the strong adhesion.

Polymer–Polymer Adhesion. Adhesion tests similar to those discussed above were performed between all combinations of PCTFE–OH, PCTFE–OC(O)NH$(CH_2)_3$Si(OEt)$_3$, and PCTFE–OC(O)NH$(CH_2)_3$Si(O)OH. No strong adhesion occurred between any of the film samples, but impressive differences were observed. Two PCTFE–OH samples do not adhere to one another, they fall apart. The other combinations form adhesive joints that are weak relative to PCTFE–OC(O)NH$(CH_2)_3$Si(OEt)$_3$–glass, and the films can be separated by modest pressure, indicating apparent adhesive failures.

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(10) PCTFE–OH does not react with $H_2N(CH_2)_3Si(OEt)_3$ in THF at room temperature for 4, h as evidenced by XPS, ATR IR, and contact analyses.

Stereospecific Polymerization of Styrene Giving the Syndiotactic Polymer

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ABSTRACT: A mixture of titanium compounds ($TiCl_4$, $Ti(OEt)_4$, or $(\eta\text{-}C_5H_5)TiCl_3$) with methylaluminoxane catalyzes the polymerization of styrene, even above room temperature, to the pure syndiotactic polystyrene, which has a narrow molecular weight distribution ($M_w/M_n = 2$). Pure syndiotactic polymers are also obtained with ring-substituted styrenes. Monomer reactivity is enhanced by electron-releasing substituents on the aromatic ring.

Introduction

The control of stereoregularity is of practical importance in the development of new polymers or tailor-made polymers and in the control of polymer properties. Since the discovery of the Ziegler–Natta catalyst systems in the early 1950s, extensive studies concerning the stereospecific polymerization of olefins have been carried out.[1,2] In most cases, isotactic polymers are obtained, and syndiotactic polymers are rare.

In principle, polystyrene can occur with isotactic, atactic, or syndiotactic configurations, but the latter was unknown until very recently.[3,4]

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